

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Production of High Dielectric Ceramics

We, NIPPON TELEGRAPH AND TELEPHONE PUBLIC CORPORATION, a Japanese Body Corporate of 1, 1-chome, Uchisaiwaicho, Chiyodaku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing a high dielectric constant ceramic of barium titanate or barium titanate solid solution series composition having an insulating layer along crystal grain boundaries, which ceramic is most adapted for use as a dielectric material for a super high frequency by-pass capacitor.

As a capacitor of the type described, the intergranular barrier layer capacitor is known to the art. (R. M. Glaister's British Patent No. 839,938 and United States Patent No. 3,028,248 which both relate to a same invention). Also, a method of producing high dielectric constant ceramics of the above-said type is disclosed in the present inventor's British Patent No. 1,047,057.

The former takes the advantage of the phenomenon that when a porous ceramic body of a high dielectric constant formed of a high purity ceramic material is made semiconductive by reduction and re-oxidized in an oxidizing atmosphere, an insulating layer is formed along the crystal grain boundaries close to the pores. According to the former method, a ceramic dielectric with a dielectric constant of the order of 100,000 or higher can be obtained, but the method still has disadvantages. Since the use of a porous body is essential, the product cannot have enough moisture proof characteristics for practical applications, and because of incomplete insulation provided by the insulating layer the working voltage is lowered and frequency

characteristics of the product are deteriorated.

The latter method, if adopted from the very outset of preparing materials for the ceramic composition, would call for a number of process steps including the first firing step for preparing a semiconductive ceramic body, an ensuing step of depositing a metallic compound on the sintered ceramic body, and a second firing step for providing a boundary insulation. According to the method, a finely sintered high dielectric constant ceramic is obtained with consequently improved moisture-proof characteristics, working voltage, and frequency characteristics. However, it again has a drawback in that when a high dielectric constant ceramic body of solution series composition having good electrical characteristics is used in order to obtain a high dielectric constant (say, of the order of 100,000 or more), the specific resistivity is lowered (to  $10^8 \Omega\text{-cm}$  or less).

According to the present invention there is provided a method of producing a barium titanium series ceramic of high dielectric constant, which method comprises adding to the constituent raw materials of a barium titanate series semiconductive ceramic 0.6 to 5.0 atomic % of an additional substance or substances comprising at least one compound containing one of the elements V, Cr, Mn, Fe, Co, Ni, Cu, As, Sb, Bi, and Tl or a mixture thereof, making into a shape, firing the shape in a gaseous atmosphere substantially free from oxidizing substance at a temperature of  $1100^\circ$  to  $1500^\circ$  C. in accordance with a first temperature programme, and thereafter firing the shape in an oxidizing atmosphere containing a volume of oxygen the partial pressure of which is at least  $1/100$ th atmosphere at a temperature of  $600^\circ$  to  $1150^\circ$  C. in accordance with a second temperature programme, said first-mentioned gaseous atmos-

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where being substantially replaced with said second-mentioned oxidizing atmosphere at a temperature of at least 600° C., whereby an insulating layer substantially consisting of a composition of said barium titanate series ceramic and ingredient elements of said additional substance or substances is formed along crystal grain boundaries throughout said ceramic, said grain size being at least 20 microns.

The constituent raw materials may include commercial grading barium titanate.

The first-mentioned atmosphere may be an inert atmosphere, preferably nitrogen, neon, argon, helium or a mixture thereof.

Alternatively, the first-mentioned atmosphere may be a reducing atmosphere such as carbon monoxide, hydrogen or a mixture thereof.

This atmosphere may in fact be a mixture of reducing and inert gases.

The first-mentioned atmosphere, in all cases of its composition, should preferably be at a pressure of 1 atmosphere absolute.

It should be noted that the substance forming an insulating layer along crystal grain boundaries of barium titanium is hereinafter referred to as "insulating layer forming material".

The expression "barium titanate series ceramics" as used herein means both a single composition of barium titanate ceramic and solid solution series ceramics made of commercial grade or high purity barium titanate and one, or a mixture of two or more, salts selected from the group consisting of (a) titanates of alkaline earth metals other than barium, (b) zirconates and stannates of alkaline earth metals, and (c) titanates, zirconates, and stannates of lead, bismuth, and antimony. In the constituent raw materials of barium titanate series ceramic as above described, the individual compositions of the solid solution series ceramics may be included singly or in the form of powder of solid solution series ceramic calcined beforehand or as a combination thereof.

The constituent raw materials for use in the manufacture of barium titanate series semiconductive ceramics are a mixture of commercial grade or high purity barium titanate or a composition for forming a barium titanate series ceramic as a base material, SiO<sub>2</sub> as an accelerator and additional components consisting of (a) one of rare earth elements from La to Lu in a periodic table or Y which substitutes parts of the Ba-sites of the unit crystal lattice of the ceramic with trivalent ions, or Ag or K which substitutes the same with monovalent ions, (b) Sb, Bi, Nb or Ta which substitutes part of the Ti site of the unit crystal lattice of the ceramic with trivalent or pentavalent ions, or (c) F or Cl which substitutes part of O-site of the unit crystal lattice of the ceramic with mono-

valent ions, or a compound containing any such element, or a mixture thereof.

As used herein the term commercial grade barium titanate means, for example, barium titanate with a purity of about 98.7% which contains approximately 0.1% by weight of Na and impurities of many other kinds.

The insulating layer forming materials are, for example, elements such as V, Cr, Mn, Fe, Co, Ni, Cu, As, Sb, Bi, Tl, or oxides thereof, or compounds which are readily converted by thermal decomposition into oxides of the above elements such as carbonates, hydroxides and nitrates thereof or oxygen-containing compounds such as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, and BaMnO<sub>4</sub>. These insulating layer forming materials may be added either singly or in a mixture of two or more. The overall amount of such materials to be added should not be too small because the addition becomes ineffective, nor should be excessively large because it entails an increase in the loss angle and other unfavorable effects. A suitable amount must therefore be chosen depending upon the types of the constituent raw materials and additional substances to be employed. Thus, inasmuch as the overall amount of the materials to be added is empirically decided upon in the light of the types and combinations of the constituent raw materials and additional substances used in practicing the method of the invention, it is impossible to define the range in definite way. A generally preferable range, nevertheless, is approximately between 0.6 to 5 atomic % on the basis of the total mol. number of the particular ceramic composition.

The constituent raw materials prepared in the way described above are formed together, and the resulting form is fired within an inert or reducing atmosphere which is substantially free from oxidizing agents at a temperature of from 1100° to 1500° C. in accordance with a first predetermined temperature controlling programme, whereby the composition is turned into a semiconductive ceramic. During this process, the composition of the inert or reducing atmosphere as mentioned above may be suitably changed.

The ceramic, thus made semiconductive, is then allowed to cool off from the firing temperature in accordance with a second predetermined temperature controlling programme, and in the meantime the atmosphere within the oven is replaced by an oxidizing atmosphere. At this time, while the reducing atmosphere in the oven may be continuously replaced by the oxidizing atmosphere, it is preferred that the oven is first evacuated by a vacuum device and then is filled with an oxidizing atmosphere.

In order to obtain a desirable insulating layer, it is important that the replacement of an inert or reducing atmosphere by an

oxidizing atmosphere should be carried out while the oven temperature is at least 600° C., preferably in excess of 700° C. While the oxidizing atmosphere may be any atmosphere which contains gaseous oxygen and is preferably kept at a pressure of about 1 atm. absolute, it must be noted that if the amount of oxygen is unduly small then no satisfactory crystal grain boundary insulation will result and the specific resistivity will drop as shown in Table 1. For this reason, the oxygen pressure must be not less than 1/100th of an atmosphere.

The formation of a crystal grain boundary insulating layer in the oxidizing atmosphere may be accomplished not only in the course of the uniform cooling of the oven but by maintaining the ceramic at a certain temperature between 600° and 1150° C. for a predetermined period, say from 20 minutes to 5 hours, during the course of the oven cooling. Alternatively, the ceramic may be cooled to room temperature while in the inert, or reducing, atmosphere and then subjected to the heat treatment in the oxidizing atmosphere.

		Specific resistivity
30	O <sub>2</sub>	$1 \times 10^{11} \Omega\text{-cm}$
	N <sub>2</sub> + O <sub>2</sub>	$3.6 \times 10^{10}$
	N <sub>2</sub> + $\frac{1}{4}$ O <sub>2</sub>	$1.0 \times 10^{10}$
	N <sub>2</sub> + $\frac{1}{20}$ O <sub>2</sub>	$1.0 \times 10^{10}$
	N <sub>2</sub> + $\frac{1}{100}$ O <sub>2</sub>	$2.0 \times 10^8$

In Table 1 there are shown specific resistivity values of ceramic specimens obtained by adding 1.4 mol. % of CuO and 0.4 mol. % of SiO<sub>2</sub> to the constituent raw materials for barium titanate series semiconductive ceramic, shaping the mixture altogether, firing the shape in nitrogen atmosphere at 1400° C. for 4 hours thereby making said shape semiconductive, and cooling the semiconductive ceramic down to a room temperature and thereafter keeping the ceramic specimens in atmospheres having different oxygen contents at about 1000° C. for one hour and finally allowing the specimens to cool down to a room temperature over a period of 12 hours.

While it is not exactly known yet for what reason even the barium titanium series semiconductive ceramic material which is apt to be

finely sintered is adequately insulated along the crystal grain boundaries by the method of the invention, we may qualitatively presume that the following is responsible. At the crystal grain boundaries of the ceramic body a solid solution of barium titanate and ions of the elements of insulating layer forming material is produced and, as the result, the diffusion velocity of oxygen along the crystal grain boundaries is accelerated and the crystal grain boundaries are easily oxidized. Thus, a high dielectric constant ceramic in which an insulating layer of substantial barium titanate compound composition containing the ions of said elements is formed throughout the ceramic along the crystal grain boundaries of the ceramic crystal grains the inside of which remains semiconductive. When the grain size of the sintered ceramic is too small, a desirable result will not be obtained as the oxidation will be limited to take place only along the surface of the ceramic. Therefore, the grain size of the sintered ceramic is preferably at least 20 microns.

Although the present invention has been described in connection with an embodiment thereof, it should be noted that the properties of the high dielectric constant ceramic to be obtained by the method of the invention depend upon conditions, such as the composition of constituent raw materials and types and amounts of elements or compounds to be added, upon conditions for heat treatment such as firing temperature, time and atmosphere, and upon grain size of fired ceramic. These conditions must be suitably chosen for the particular purpose intended, as will be understood from the examples of the invention which are given hereunder.

The present invention is illustrated by the following examples, in which all the atmospheres are at a pressure of 1 absolute atm. and the compositions thereof are expressed by volume.

#### EXAMPLE 1

To commercial grade barium titanate were added 0.1 mol. % of Dy<sub>2</sub>O<sub>3</sub> (dysprosium oxide), 0.4 mol. % of SiO<sub>2</sub> and 1.5 mol. % of CuO, and the constituent raw materials were made into a shape together. The shape was then subjected to heat treatment under conditions of:

Room temp.—1400° C. (in N<sub>2</sub> atmosphere), kept at 1400° C. for 4 hrs. (in mixed atmosphere of N<sub>2</sub>+1% H<sub>2</sub>), and 1400° C.—room temp. (in mixed atmosphere of N<sub>2</sub>+1/4 O<sub>2</sub>)

The dielectric characteristics of the ceramic thus obtained with an average grain size of about 40 were: dielectric constant ( $\epsilon$ ) 30,000; loss angle ( $\tan \delta$ ) 4.5%; specific resistivity

( $\rho$ )  $2.0 \times 10^{10} \Omega\text{-cm}$ ; and, dielectric strength (vs) 1000 V/mm.

#### EXAMPLE 2

The same constituent raw materials as in Example 1 were shaped altogether, and the shape was heat treated under the following conditions:

Room temp.—1400° C. ( $N_2$ ), kept at 1400° C. for 4 hrs. ( $N_2 + 1\% H_2$ ), and 1400° C.—room temp. ( $N_2 + 1/20 O_2$ )

The dielectric properties of the ceramic so obtained with an average grain size of about 40  $\mu$  were:  $\epsilon = 34,000$ ;  $\tan \delta = 5.8\%$ ;  $\rho = 2.5 \times 10^9 \Omega\text{-cm}$ ; and,  $V_s = 700$  V/mm.

#### EXAMPLE 3

To commercial grade barium titanate were added 0.1 mol. % of  $Dy_2O_3$ , 0.4% mol. % of  $SiO_2$ , and 0.1 mol. % of  $MnO_2$ , and the mixture of constituent raw materials was shaped. Then, the shaped was heat treated under the same conditions as in Example 1. The dielectric characteristics of the ceramic which resulted with an average grain size of about 40  $\mu$  were  $\epsilon = 39,000$ ;  $\tan \delta = 4.1\%$ ;  $\rho = 5.5 \times 10^9 \Omega\text{-cm}$ ; and  $V_s = 700$  V/mm.

#### EXAMPLE 4

To commercial grade barium titanate were added 0.1 mol. % of  $Dy_2O_3$ , 0.4 mol. % of  $SiO_2$  and 1.5 mol. % of  $Ti_2O_3$ , and the constituent raw materials were shaped altogether. The resulting shape was heat treated under the conditions of:

Room temp.—1400° C. ( $N_2$ ), kept at 1400° C. for 4 hrs. ( $N_2$ ), and 1400° C.—room temp. ( $N_2 + O_2$ )

The dielectric characteristics of the ceramic thus obtained which had an average grain size of about 40  $\mu$  were  $\epsilon = 30,000$ ;  $\tan \delta = 5.2\%$ ;  $\rho = 1.6 \times 10^{10} \Omega\text{-cm}$ ;  $V_s = 1000$  V/mm.

#### EXAMPLE 5

To commercial grade barium titanium were added 10 mol. % of barium stannate, 0.1 mol. % of  $Dy_2O_3$ , 0.4 mol. % of  $SiO_2$ , and 0.5 mol. % of  $CuO$ , and the mixture was shaped altogether, and then the shape was heat treated under the conditions of:

Room temp.—1400° C. ( $N_2$ ), kept at 1400° C. for 4 hrs. ( $N_2$ ) and 1400° C.—room temp. ( $N_2 + 1/4 O_2$ ).

The ceramic thus obtained with an average grain size of about 55  $\mu$  had the following dielectric characteristics:  $\epsilon = 84,000$ ;  $\tan \delta = 5.0\%$ ;  $\rho = 1.0 \times 10^{10} \Omega\text{-cm}$ ; and  $V_s = 350$  V/mm.

#### EXAMPLE 6

To commercial grade barium titanate were added 10 mol. % of barium stannate, 0.1 mol. % of  $Dy_2O_3$ , 0.4 mol. % of  $SiO_2$ , and 0.9 mol. % of  $CuO$ . The mixture was shaped altogether, and then the shape was heat treated under the conditions of:

Room temp. 1450° C. ( $N_2$ ), kept at 1450° C. for 4 hrs. ( $N_2$ ), and 1450° C.—room temp. ( $N_2 + 1/4 O_2$ ),

The ceramic thus obtained had an average grain size of about 60  $\mu$  and exhibited the following dielectric characteristics:  $\epsilon = 120,000$ ;  $\tan \delta = 15\%$ ;  $\rho = 1.0 \times 10^{10} \Omega\text{-cm}$ ; and  $V_s = 300$  V/mm.

As exemplified by the foregoing Examples, the present invention provides a method of producing a ceramic, of a high dielectric constant, having a substantially complete insulating layer along the crystal grain boundaries throughout the firedly sintered body, from the surface to the inside. As a consequence of this insulating layer, the moisture-proof characteristics of the ceramic and the electrical properties such as working voltage, frequency characteristics and loss angles, can be improved.

As also exemplified by the Examples, the invention provides a method effectively applicable to the manufacture of a solid solution series high dielectric constant ceramic. By the method of the invention such a ceramic is obtained which exhibits excellent electrical properties such as good working voltage and frequency characteristics and high specific resistivity. The ceramic obtained hereby also exhibits good moisture-proof characteristics.

The method of the invention as exemplified also enables a ceramic to be economically and efficiently manufactured by a reduced number of process steps.

Furthermore, the method of the invention as exemplified permits the use of commercial grade ceramic material, containing impurities, as well as the use of high purity ceramic material. The method, therefore, facilitates a cheaper manufacture of high dielectric constant ceramics.

#### WHAT WE CLAIM IS:—

1. A method of producing a barium titanate series ceramic of high dielectric constant which method comprises adding to the constituent raw materials of a barium titanate series semiconductive ceramic 0.6 to 5.0 atomic % of an additional substance or substances comprising at least one compound containing one of the elements V, Cr, Mn, Fe, Co, Ni, Cu, As, Sb, Bi, and Tl or a mixture thereof, making into a shape, firing the shape in a gaseous atmosphere substantially free from oxidizing substance at a tempera-

- ture of 1100° to 1500° C. in accordance with a first temperature programme and thereafter firing the shape in an oxidising atmosphere containing a volume of oxygen the partial pressure of which is at least 1/1000th atmosphere at a temperature of 600° to 1150° C. in accordance with a second temperature programme, said first-mentioned gaseous atmosphere being substantially replaced with said second-mentioned oxidising atmosphere at a temperature of at least 600° C., whereby an insulating layer substantially consisting of a composition of said barium titanate series ceramic and ingredient elements of said additional substance or substances is formed along crystal grain boundaries throughout said ceramic, said grain size being at least 20 microns.
2. A method as claimed in claim 1, wherein said constituent raw materials include commercial grade barium titanate.
3. A method as claimed in claims 1 or 2, wherein said first-mentioned atmosphere is at a pressure of 1 atmosphere absolute.
4. A method as claimed in claims 1, 2 or 3, wherein said first-mentioned atmosphere is at inert gas.
5. A method as claimed in claims 1, 2 or 3, wherein said first-mentioned atmosphere is a reducing gas.
6. A method as claimed in claims 1, 2, 3 or 4, wherein said first-mentioned atmosphere is nitrogen, argon, neon, helium, or a mixture thereof.
7. A method as claimed in claims 1, 2, 3 or 5, wherein said first-mentioned atmosphere is hydrogen, carbon monoxide or a mixture thereof.
8. A method as claimed in claims 1, 2 or 3, wherein said first-mentioned atmosphere is a mixture of inert and reducing gases.
9. A method as claimed in any preceding claim, wherein said mixture of said constituent raw materials and said additional substance or substances is calcined in an inert or reducing atmosphere and pulverized before shaping.
10. A method of producing a barium titanate series ceramic of a high dielectric constant substantially as hereinbefore described with reference to any one of the foregoing Examples.
11. A ceramic when made by the method as claimed in any preceding claim.

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